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# Aquatic Chemistry of Selenium: Evidence of Biomethylation†

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■ The chemical species of dissolved selenium were examined in surface waters from three sites in the San Joaquin and Imperial Valleys of California. Six dissolved selenium species were identified: the inorganic species selenate and selenite; nonvolatile organic selenides, including seleno amino acids and a dimethylselenonium ion; and the volatile methylated forms dimethyl selenide and dimethyl diselenide. The occurrence of methylated selenium species in the aquatic environment has important implications regarding the biogeochemical behavior of selenium in natural aqueous systems. Laboratory studies indicate that the nonvolatile dimethylselenonium ion can be transformed into volatile dimethyl selenide at neutral pH, providing a pathway for the in situ production of dimethyl selenide in natural waters. Geochemical flux calculations indicate that outgassing of dimethyl selenide may be an important removal mechanism for dissolved selenium from aqueous systems.

## *Introduction*

Selenium is highly enriched in atmospheric aerosols relative to its crustal abundance (enrichment factor relative to crust, $EF_{Al}$ = 1000–6000), and a large fraction of atmospheric selenium appears to exist in an unidentified vapor phase (*1*, *2*). Biomethylation of selenium followed by release of volatile dimethyl selenide to the atmosphere has been proposed as a pathway for the atmospheric enrichment of selenium (*1*). Because the surface ocean has recently been postulated to be a major source of vapor-phase selenium to the atmosphere (*3*), biomethylation of selenium in surface waters may be important on a global scale.

Despite the postulated importance of this process on a global basis, little data exist demonstrating that alkyl selenides are produced in surface waters of natural systems. Nevertheless, some indirect evidence supports this hypothesis. Dimethyl selenide and dimethyl diselenide have been observed emanating from plants (*4*), soils (*5*), and laboratory cultures of aqueous suspensions of sewage sludge, soil, and lake sediment (with and without added inorganic selenium) (*6*, *7*). Alkyl selenides have also been detected in the atmosphere just above a freshwater lake (*8*).

The aquatic chemistry of selenium is complicated since it can exist in four different oxidation states and as a variety of inorganic and organic compounds. Dissolved inorganic selenium can exist in natural waters as Se(–II), primarily as biselenide ($HSe^-$); Se(0), as colloidal elemental selenium; Se(IV), as the selenite oxyanion ($HSeO_3^-$ and $SeO_3^{2-}$); and Se(VI), as the selenate oxyanion ($SeO_4^{2-}$). Organic forms of selenium are analogous to those of sulfur and include seleno amino acids and their derivatives, methyl selenides, methyl seleninic esters, methyl selenones, and methylselenonium ions. The pathways for the biotransformation of inorganic Se to the various organic forms and the interconversion between these different molecular species of selenium are not well understood.

At present, there are few analytical methods available that can isolate and quantify the broad spectrum of biogeochemically imporant selenium species (noted above) that may be present in natural water systems. To address this concern, we developed a procedure that enabled the measurement of both volatile alkyl selenide species and their precursors as well as other inorganic and organic forms of selenium. Although other methods have been reported for the sampling and analysis of alkyl selenides (*6–8*), our procedure involving in-field cryogenic trapping with subsequent laboratory separation/detection via thermal-gradient gas chromatography (GC)/gas-phase atomic absorption (AA) allowed interfacing with methods used for the determination of inorganic selenium species (*9*). This paper reports the results obtained on the distribution of dissolved selenium species in two lakes and one river in the San Joaquin and Imperial Valleys of California, all of which receive agricultural drainage. The results provide insight into the biogeochemical cycling of selenium in natural waters.

## *Experimental Section*

**Sampling Sites.** Three natural aqueous systems in California were selected for the examination of dissolved selenium species. These systems are environments in which we believed the presence of methylated selenium species might be detected. System 1, the Kesterson National Wildlife Refuge (Kesterson Reservoir), is a marsh in the western San Joaquin Valley. During this study, the Kesterson Reservoir received agricultural drainage waters containing extremely high concentrations of dissolved selenium (ca. 4 μM) from the San Luis Drain (SLD). The elevated selenium in the agricultural drainage water originates from weathering of selenium-rich marine shales in the surrounding hills, which resulted in the deposition of high levels of selenate in the soils along the Panoche Fan formation located in the western edge of the San Joaquin Valley. The SLD water is delivered to ponds 1 and 2 of the Kesterson Reservoir. The water then flows sequentially through a series of 12 evaporation ponds. System 2, five sites along the San Joaquin River (Figure 1), was chosen because this river is a route for the removal of excess agricultural drainage waters from the San Joaquin Valley to the Sacramento–San Joaquin River Delta and San Francisco Bay. System 3, the Salton Sea in the Imperial Valley of southern California, is a saline lake that also receives agricultural drainage water. However, due to the absence of major outcrops of selenium-rich marine shales in the surrounding hills, the irrigated soils have lower selenium concentrations.

Surface water was collected from the Kesterson Reservoir during two visits (February 1985 and May 1986), while oxic groundwater was sampled in June 1986. Groundwater was also sampled from another site in the western San Joaquin Valley near Mendota. Surface waters were sampled from the five sites along the San Joaquin River and from three depths in the Salton Sea.

**Sampling Techniques.** Procedures were developed for sampling and storage of volatile methylated selenium compounds (methyl selenides) and dimethylselenonium ions ($DMSe^+$–R) that minimized loss and interconversion of these reactive compounds (Figure 2). The procedures involved in-field purging and cryogenic trapping of volatile compounds on glass columns packed with silanized glass

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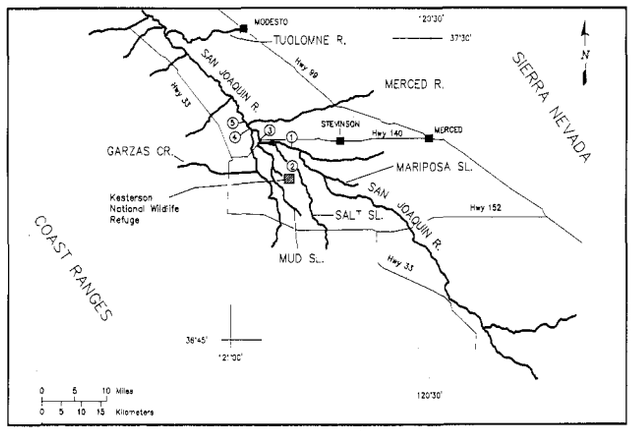


**Figure 1.** San Joaquin River sampling site locations.

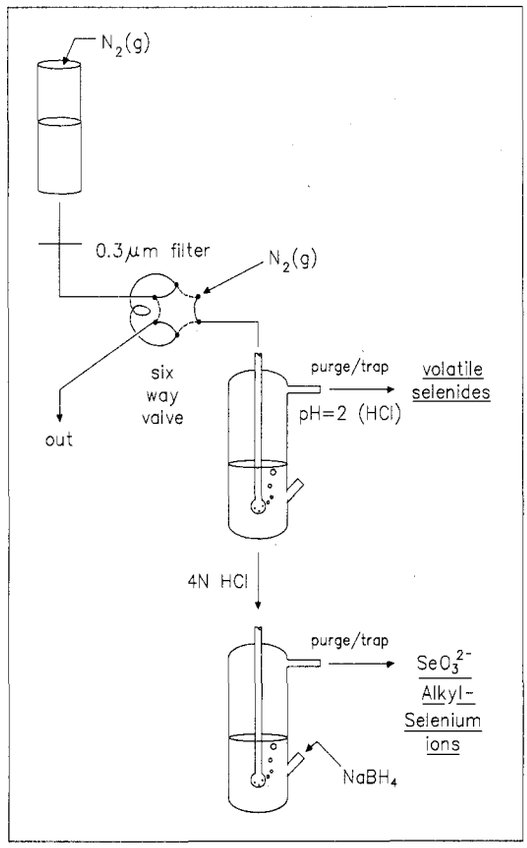


**Figure 2.** Apparatus for sampling alkyl selenium compounds.

beads and immersed in liquid nitrogen. Initial studies using 10 ng of diethyl selenide as an internal standard to assess the efficiency and stability of the in-field trapping technique demonstrated >95% recovery after storage of the traps for up to 3 days in liquid nitrogen. Water samples were collected in a Plexiglas vessel taking great care to minimize turbulence. Water samples were immediately filtered through a 0.3-μM polycarbonate membrane filter (Nucleopore) with a Teflon filter sandwich. Several aliquots were drawn with use of a six-way Telfon valve. Sample aliquots were acidified to pH 2 (Baker HCl) to minimize conversion of $DMSe^+$–R to dimethyl selenide (DMSe) during stripping of volatile selenides (Figure 3).

For the collection of nonvolatile methylated selenium compounds, aliquots that had been previously stripped of volatile methyl selenides were acidified to 4 M with HCl (Baker) and reacted with 4 mL of 3% $NaBH_4$ over 7 min to produce volatile selenide derivatives, which were then

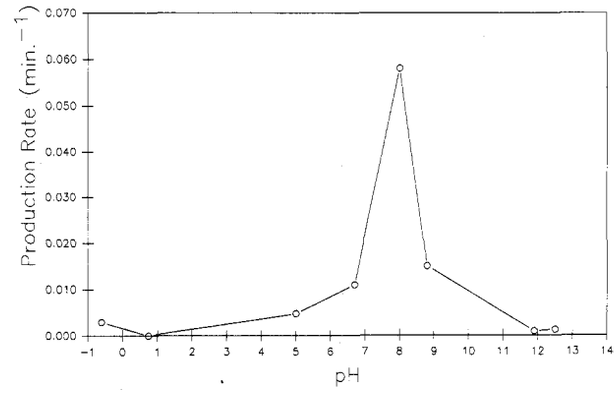


**Figure 3.** pH dependence of the production of DMSe from $DMSe^+$–R during purging. $DMSe^+$–R was isolated from surface water samples collected from Kesterson Reservoir on May 13, 1986, on Dowex AG50 cation-exchange resin (see text).

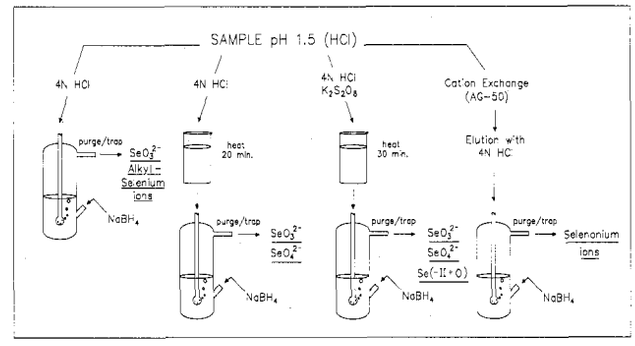


**Figure 4.** Analytical procedure for selenium speciation determinations.

stripped and trapped. For the less reactive species (e.g., selenate and selenite), samples were stored refrigerated (after acidification to pH 1.5 with HCl) in acid-cleaned, silanized, borosilicate glass bottles with Teflon-lined caps until analysis (<60 days).

**Analysis.** Selenium speciation measurements were carried out according to a modification of procedures described by Cutter (*10*, *11*) and Cutter and Bruland (*9*) (Figure 4). Samples were purged with $N_2(g)$ and the volatile selenium compounds trapped on a 25-cm glass column packed with 5% OV 3 on Chromosorb WHP (80–100 mesh) at liquid nitrogen temperature. Controlled warming of the column from −196 to 100 °C over 4 min sequentially distilled and separated the trapped selenides, which were then detected by gas-phase flame atomic absorption spectrometry (absolute detection limit = 0.1 ng or 1 pmol of Se). Since the reducing reagent $NaBH_4$ does not cleave selenide–carbon bonds or reduce selenate in 4 M HCl, it was used to selectively reduce selenite to hydrogen selenide gas. This reagent also reduces oxidized methylated selenium compounds (e.g., dimethyl selenone, methaneseleninic acid, and dimethylselenonium compounds) to their corresponding methylated selenide derivatives (e.g., dimethyl selenide, methylselenol, and dimethyl selenide, respectively) (*12*). Cation-exchange separation techniques (*13*) were utilized to separate dimethylselenonium ions ($DMSe^+$–R) from dimethyl selenone ($DMSeO_2$) or dimethyl selenoxide (DMSeO), since both of these forms were reduced to the same selenide. Selenate plus selenite concentrations were determined after first reducing the selenate to selenite with hot 4 M HCl followed by $NaBH_4$ reduction. The concentration of selenate was calculated from the difference between the selenate plus selenite and selenite concentrations. Total nonvolatile dissolved selenium ($Se_{TNV}$) was determined by oxidizing all of the dissolved nonvolatile selenium species

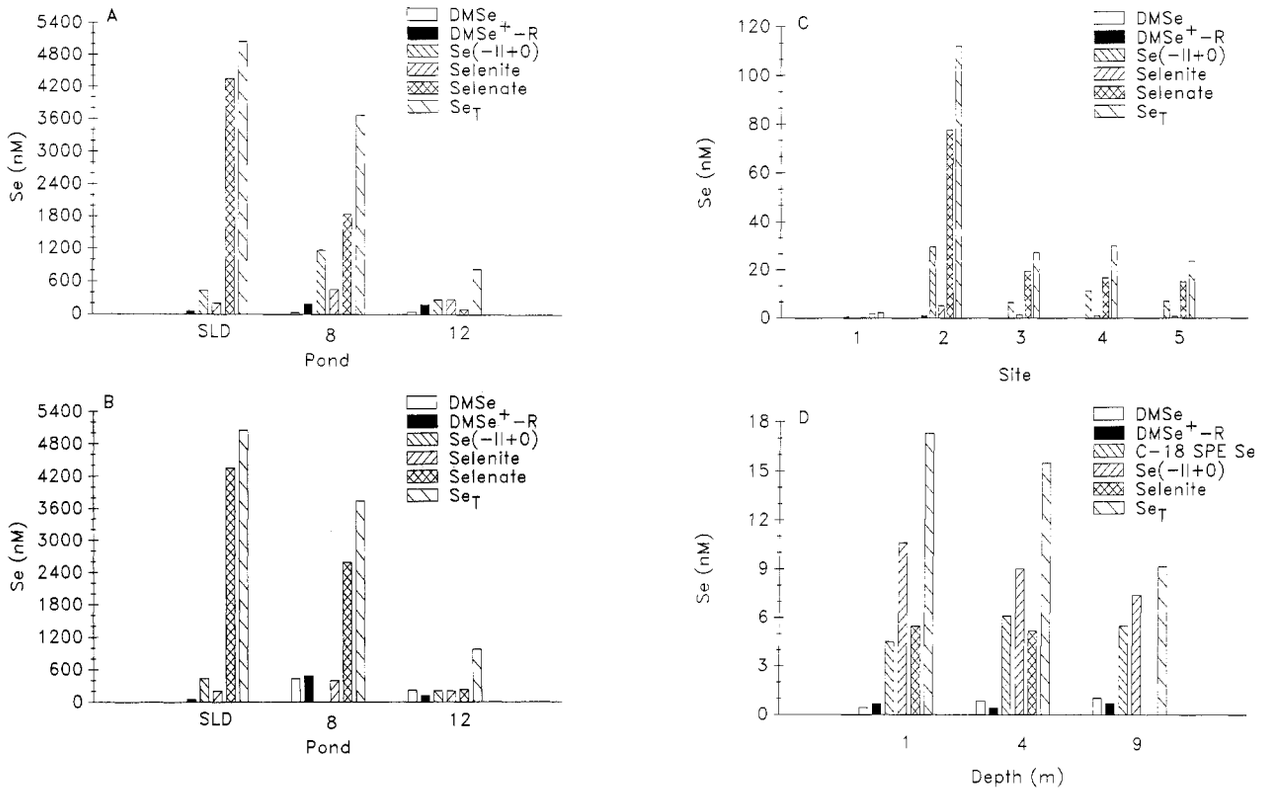


**Figure 5.** Selenium speciation results: (A) Kesterson Reservoir, February 28, 1985; (B) Kesterson Reservoir, May 13, 1986 (SLD data from February 28, 1985, given as reference); (C) San Joaquin River, September 10, 1986 (stations 1 and 2), and September 24, 1986 (stations 3–5); (D) Salton Sea, October 8, 1986.

to selenate with potassium persulfate and subsequent reduction of the selenate to selenite for analysis. Soluble organic selenides, which were not reduced by $NaBH_4$, (e.g., selenocysteine, selenomethionine, and soluble peptides and proteins containing these amino acids), together with any colloidal elemental selenium are included in the $Se_{TNV}$ fraction but not in the selenate plus selenite fraction. Therefore, the difference between these two fractions was used to obtain the concentration of dissolved organic plus elemental selenium, Se(−II+0). Total selenium ($Se_T$) was calculated by addition of the concentrations of DMSe, DMDSe, and $DMSe^+$–R to $Se_{TNV}$.

To directly estimate the amount of selenium existing as soluble organic selenides and associated with dissolved organic matter, acidified (pH 1.5) water samples were passed through a C-18 solid-phase extraction (SPE) column (Sep-Pak, Waters Assoc.) and rinsed with acidified (pH 1.5) glass distilled water, and the organic material was eluted with 3 mL of HPLC-grade methanol. The methanol eluates were evaporated to dryness, and the residue was dissolved in acidified glass distilled water (pH 1.5) and analyzed for total selenium. The C-18 SPE appeared to quantitatively isolate dissolved organic selenides that could be associated with soluble peptides, proteins, and higher molecular weight organic compounds. However, the C-18 SPE technique did not appear to quantitatively recover selenium-containing free amino acids, such as selenomethionine. In acid solution these free amino acids are apparently too polar, possibly due to the protonation of the amine functional group, to be quantitatively retained by the nonpolar C-18 coated resin. Thus, any difference between the Se(−II+0) and C-18 SPE fractions can be attributed to the presence of colloidal elemental selenium and/or selenium-containing free amino acids.

The relative analytical precision of the technique for species or fractions that were determined directly (selenite, DMSe, DMDSe, $DMSe^+$–R, and C-18 SPE Se) is approximately ±5% as determined by replicate analysis of standards (or samples for $DMSe^+$–R and C-18 SPE Se). The relative analytical precision for the species/fractions that were determined by difference [Se(VI), Se(−II+0)] depended on the concentrations of the various fractions in each particular sample and averaged approximately ±10%.

Due to the absence of an analytical blank, the relative detection limit for the methylated species, all of which are determined directly, depended on the sample volume that was analyzed. For a 100-mL sample, the detection limit for the methylated species was 0.01 nM. The detection limit for selenite was limited by the variability in the analysis blank. Cutter (*10*) reported a detection limit of 0.02 nM for selenite with a 100-mL sample volume. The relative detection limit for species that were determined by difference [selenate and Se(−II+0)] was determined by the absolute error associated with the determination of the concentration of the other species/fractions (e.g., selenate plus selenite, selenite, $Se_{TNV}$) that were used to calculate the concentrations of selenate and Se(−II+0) and generally were >0.03 nM for a 100-mL sample.

## *Results*

**Kesterson Reservoir.** Surface water samples from the SLD input and Kesterson Reservoir ponds 8 and 12 collected on February 28, 1985, contained detectable amounts of five dissolved forms of selenium: selenate, selenite, Se(−II+0), DMSe, and $DMSe^+$–R (Figure 5A). $Se_T$ in pond 12 was only 12% of the $Se_T$ in the SLD. The decrease in $Se_T$ through the evaporation ponds results largely from a dramatic decrease in selenate concentrations. Initially, selenate comprised 90% of the $Se_T$ in the SLD feed water. However, in pond 12 (the last in the sequence of evaporation ponds) selenate made up only 10% of the $Se_T$. Within the biologically active Kesterson Reservoir marsh system, the concentration of dissolved organoselenium

**Table I. Selenium Speciation in San Joaquin Valley Groundwater**

| sample location | date | nM as Se | | |
|---|---|---|---|---|
| | | DMSe | DMDSe | $DMSe^+$–R |
| Kesterson Pond 2, 36′ well | 6/3/86 | 943 | 38.3 | 271 |
| Mendota subsurface groundwater | 5/28/86 | 130 | 13.2 | |

species increased along the pond sequence; the two methylated selenium compounds DMSe and $DMSe^+$–R respresented 6% and 21% of the $Se_T$, respectively, in pond 12.

Analysis of samples obtained during a more recent visit (May 1986) utilizing in-field trapping procedures to isolate the volatile and methylated compounds revealed higher concentrations of DMSe and $DMSe^+$–R ranging from 12 to 22% and from 12 to 13%, respectively, of the $Se_T$ in the Kesterson Reservoir ponds (Figure 5B). DMSe was the major volatile selenium species, constituting greater than 99.8% of the total volatile selenium present. Dimethyl diselenide (DMDSe) comprised from 0.1 to 0.2% of the total volatile selenium. Hydrogen selenide was not detected in any samples (<0.2 nM). Oxic groundwater contained elevated levels of methylated selenium compounds compared to the surface waters, with DMDSe representing 4 and 9% of the total dissolved volatile selenium (Table I).

**San Joaquin River.** Selenate was the major dissolved selenium species in the San Joaquin River, constituting from 56 to 71% of the $Se_T$ (Figure 5C). Selenite comprised from 5 to 10% of the $Se_T$ while the Se(–II+0) fraction made up <14–38% of the $Se_T$. $DMSe^+$–R was present in two samples, and its concentration represented 1 and 19% of the $Se_T$. DMSe was not detected (<0.1–<3% of the $Se_T$).

**Salton Sea.** Hydrographic data from the Salton Sea were obtained from a Surveyor II CTD equipped with an $O_2$ membrane electrode (Hydrolab Corp.). The data indicated that a strong pycnocline existed at depths from 1 to 6 m. This stratification of the water column resulted in complete oxygen depletion at depths below 8 m ($O_2$ < 0.2 ppm) where the presence of $H_2S$ was noted. The majority of the $Se_T$ (58–81%) in the Salton Sea was in the Se(–II+0) fraction (Figure 5D). Selenite was 33% of the $Se_T$ in the oxic surface waters but <1% of $Se_T$ in anoxic bottom water. Selenate was not detected (<1% $Se_T$) even in oxic surface waters. DMSe comprised 2–11% of the $Se_T$ and showed increasing concentrations with depth. $DMSe^+$–R concentrations ranged from 3 to 8% of the $Se_T$. C-18 SPE Se was a major fraction (42–74%) of the Se(–II+0) with proportions increasing with depth.

*Discussion*

The aquatic species distribution of selenium observed in these freshwater systems is consistent with the marine biogeochemical selenium cycle proposed by Cutter and Bruland (*9*). This selenium cycle involves reductive assimilation of selenate and selenite by organisms to organically bound selenide, release of selenium as dissolved organic selenide upon death or depuration, and multistep oxidation of organic selenide to selenite and, eventually, selenate. The oxidation of selenite to selenate is thought to be a kinetically slow process (*9*), thereby allowing the thermodynamically unstable selenite species to persist in oxygenated waters.

Our detection of DMSe in natural aqueous systems provides direct evidence for a selenium biomethylation pathway similar to that previously proposed for sulfur (*14*). We suggest that production of DMSe occurs by transformation of biogenically derived $DMSe^+$–R to DMSe intra- and/or extracellularly (Figure 6). While the identity of the selenonium ion in solution has not been fully established, *Se*-methylselenomethionine is a likely candidate.

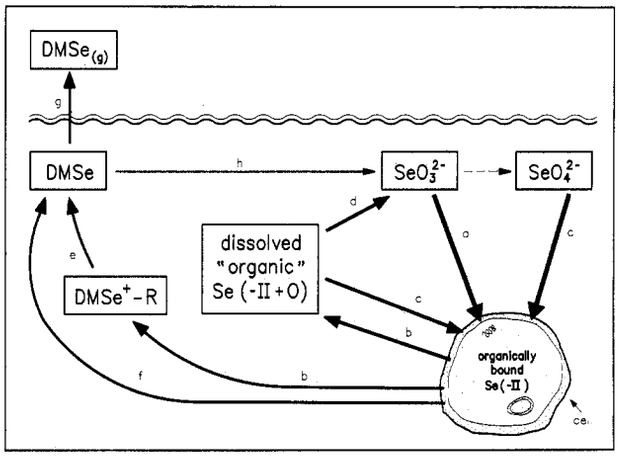


**Figure 6.** Proposed biogeochemical cycle of selenium in natural waters. Lower-case letters correspond to the following processes: (a) reductive assimilation of selenate and selenite into organically bound selenide by organisms; (b) release of organically bound selenide back to solution; (c) assimilation of dissolved organic selenide by organisms; (d) oxidation of dissolved organic selenide to selenite; (e) conversion of dissolved $DMSe^+$–R to dimethyl selenide (DMSe); (f) direct release of DMSe to solution; (g) degassing of DMSe to the atmosphere; (h) oxidation of DMSe to selenite and/or selenate.

*Se*-Methylselenomethionine has been identified as the predominant water-soluble organic selenium compound in five plant species grown on media containing both normal and elevated selenium concentrations (*15*, *16*). This compound has been proposed as the precursor of DMSe in the metabolic pathways of higher plants and marine algae (*16*, *17*). In studies with cabbage leaf enzyme extracts, Lewis et al. (*4*) proposed an enzymatically mediated pathway for the production of DMSe from *Se*-methylselenomethionine. Our results indicate a nonenzymatic pathway is also possible (Figure 7). Laboratory studies on the selenonium ion isolated from Kesterson Reservoir indicate that DMSe is produced from $DMSe^+$–R between pH 2 and pH 11 (Figure 3), probably via hydrolysis, providing a mechanism for the extracellular transformation of dissolved $DMSe^+$–R into DMSe. A similar pathway involving the plant-derived sulfonium ion (dimethylsulfonio)propionate has recently been suggested for the production of dimethyl sulfide in surface seawater by marine algae (*14*).

The existence of this selenonium ion and elevated levels of DMSe in oxic groundwater suggest release of $DMSe^+$–R from detrital plant material followed by hydrolysis to DMSe. However, direct microbial production of DMSe cannot be ruled out. Previously proposed pathways for the microbial biosynthesis of DMSe indicated that dimethyl selenone and/or methyl methane selenonate was an intermediate in microbial selenite metabolic pathways (*6*). Since no detectable levels of these soluble metabolites were observed in this study, there is no direct evidence that these microbial biomethylation mechanisms occur. If DMSe was produced by microbial biosynthesis, an alternative microbial pathway analogous to that proposed by Lewis et al. (*4*) for the biomethylation of selenite and selenate by higher plants involving a $DMSe^+$–R intermediate may be responsible (Figure 7).

The volatility of DMSe and DMDSe provides a mechanism for the outgassing of selenium from aquatic systems.

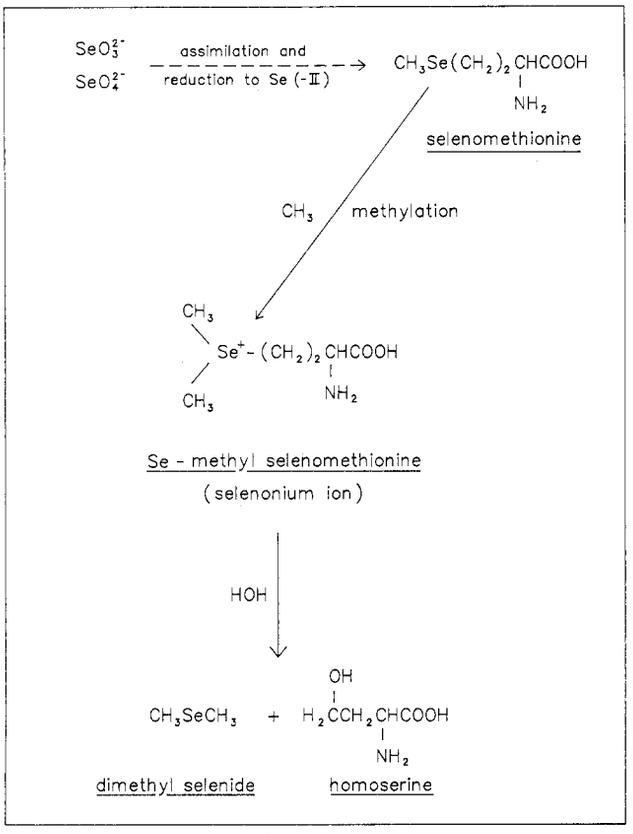


**Figure 7.** Proposed pathway for the production of DMSe in natural waters.

To determine the potential significance of the outgassing of DMSe from the surface waters of the Kesterson Reservoir to the atmosphere, an estimate of the evasion flux can be obtained from the one-dimensional, thin-layer, gas diffusion model of Liss and Slater (*18*). Assuming that (1) the oxidation or demethylation of DMSe is negligible in the surface microlayer, (2) the concentration of DMSe in overlying air is insignificant, (3) the gaseous diffusion coefficient for DMSe is similar to dimethyl sulfide ($1.0 \times 10^{-4}$ m$^2$ d$^{-1}$), (4) the microlayer thickness is 50 $\mu$m, and (5) an average dissolved DMSe concentration of 30 nM during the period in which inflow data to the pond was available (1985), the evasion flux is 6.6 $\mu$mol of DMSe m$^{-2}$ d$^{-1}$. This corresponds to a very short mean residence time for DMSe in the ponds of approximately 2 d. A mass balance using a total pond surface area of $4.8 \times 10^6$ m$^2$ and an average input of total dissolved selenium of 7.3 kg of selenium d$^{-1}$ (*19*) indicate that during this period roughly 30% of the selenium introduced into the ponds via the SLD was lost by volatilization to the atmosphere. If a DMSe concentration of 300 nM is used (the level observed during the 5/13/86 sampling trip), an evasion flux of 66 $\mu$mol of DMSe m$^{-2}$ d$^{-1}$ is estimated; a value 10-fold higher than the average observed during 1985. These results infer a substantial seasonal variability in biomethylation rates. Although a more detailed assessment of the temporal variability of these processes is needed to quantify their significance, these calculations clearly demonstrate that outgassing of selenium is substantial in the biologically active Kesterson Reservoir.

The amounts of DMSe and $DMSe^+$–R relative to the $Se_T$ found in the Salton Sea, 2–11% and 3–8% respectively, are similar to those observed in the Kesterson Reservoir. These results demonstrate that methylated selenium compounds are not limited to environments with elevated levels of selenium. The increasing concentrations of DMSe with depth in the Salton Sea most likely result from the degassing of DMSe from the surface layers, combined with accumulation in deeper waters due to restricted exchange between surface and deep waters. The absence of selenate in surface waters is particularly surprising since selenate is the thermodynamically predicted form in oxygenated waters (*9*). This observation suggests that selenate delivered to the Salton Sea has undergone reductive incorporation by organisms. The high proportion of Se(–II+0) and C-18 SPE Se observed support this hypothesis. The presence of selenite may be explained by the oxidation of reduced organic selenium compounds to selenite in the oxygenated upper 4 m of the water column. Both the slow rate of oxidation of selenite to selenate and the incorporation of selenite by organisms before it is oxidized may be factors contributing to the lack of selenate in these oxic surface waters. The decrease in $Se_T$ through the anoxic zone is indicative of selenium removal via formation of insoluble metal selenides and/or elemental selenium, consistent with previous findings in anoxic environments (*11*, *20*). Within the anoxic zone 81% of the dissolved $Se_T$ was in the Se(–II+0) fraction. The observation that 74% of the Se(–II+0) was isolated on a C-18 SPE column suggests that dissolved organoselenide compounds are the dominant form of selenium. In contrast to reduced forms of inorganic selenium [$HSe^-$, Se(0)], these organoselenides may be more water soluble, which would tend to keep selenium in solution in anoxic environments.

No detectable DMSe was observed in the San Joaquin River samples. However, the presence of $DMSe^+$–R in two upstream samples suggests DMSe may be produced, but due to the much greater turbulence in the riverine environment, gas exchange is enhanced allowing DMSe to escape rapidly. The relative proportions of the various selenium species do not vary significantly downstream of the Salt Slough input. This conservative behavior suggests that selenium species do not undergo transformations on time scales of a few hours (the time required for the water to traverse the distance between the three sites) in the riverine environment.

In contrast to the river samples, the two oxic groundwater samples exhibited extremely high levels of DMSe and DMDSe, which may be explained by both isolation of groundwater from gas exchange with the atmosphere and shielding of groundwater from ultraviolet photochemical oxidation. We did not analyze any anaerobic or anoxic groundwaters. However, on the basis of analogies with dimethyl sulfide (*21*) and recent research on the kinetics of the destruction of DMSe in anoxic sediments (*22*), alkyl selenides should not be enriched in anoxic groundwater.

## *Conclusions*

Due to limitations in previous analytical techniques and sampling/storage methodology, methylated selenium species have not been demonstrated to be an important component of the total dissolved selenium present in natural waters. Hence, biomethylation has not been recognized as an important process in the aqueous chemistry and geochemical cycling of selenium.

In the studies reported here, three dissolved methylated selenium compounds, DMSe, DMDSe, and $DMSe^+$–R, have been detected in natural water samples by an in-field cryogenic trapping technique. The presence of methylated selenium compounds in diverse natural aquatic systems suggests that biomethylation of selenium is a common process. The presence of $DMSe^+$–R suggests that the production of DMSe in aqueous systems involves hydrolysis of $DMSe^+$–R to DMSe at neutral pH. High levels

of DMSe and $DMSe^+$–R in oxic groundwater indicate that either $DMSe^+$–R is released from plant detritus and is transformed to DMSe via hydrolysis or that microbial biosynthesis of DMSe occurs via pathways involving $DMSe^+$–R.

Analysis of stored water samples, especially those obtained from biologically active regimes, may underestimate the total selenium content. Future analytical efforts will require a level of sophistication beyond total element determination in order to generate a more reliable picture of the environmental mobility and fate of selenium in aquatic systems. The Kesterson Reservoir and the Salton Sea are good examples of systems in which the dominant solution form of selenium is organoselenium compounds. Models based solely on inorganic species will not adequately describe the complexity of the aquatic chemistry of selenium in such systems. Instead, models applied to biologically active aquatic regimes should address both the occurrence and the kinetics associated with the production and removal of organic as well as inorganic selenium species.

*Acknowledgments*

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**Registry No.** Se, 7782-49-2; $H_3CSeCH_3$, 593-79-3; $H_3CSeSeCH_3$, 7101-31-7; $(H_3C)_2Se^+(CH_2)_2CH(NH_2)CO_2H$, 7728-97-4.

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# An Analysis of Precipitation Chemistry Measurements in Ontario

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■ Precipitation chemistry in Ontario from 1980 to 1983 has been assessed to understand its monthly variations and the relative importance of sulfuric and nitric acids to precipitation acidity. Except for nitrate, which has its maximum in March, parameter concentrations peaked in the summer and late spring. Nitrate contributes typically half as much acidity as sulfate on an annual basis, but in the winter months (especially for snow), the nitrate contribution is comparable to or greater than that of sulfate. Free hydrogen ion concentrations determined from laboratory pH measurements may be typically 15% lower than those from the field pH measurements. The observed neutralization of strong acids in precipitation, on the basis of laboratory pH, $SO_4^{2-}$, and $NO_3^-$, especially in late spring and summer, can be attributed to $NH_4^+$ (19–36%), $Ca^{2+}$ (10–21%), and $Mg^{2+}$ (2% or less). There is some indication of the presence of up to 17% free acids that cannot be accounted for by sulfuric and nitric acids but may be attributable to organic acids.

*Introduction*

Precipitation chemistry measurements have been made in Europe since the 1950s (*1*). In North America, continuous, large-scale measurements in the form of networks began only after the mid 1970s (*2*). In most cases, commercial wet-only samplers equipped with a moisture-activated sensor are used. The observed results have been used to examine different aspects of the acid rain phenomenon, e.g., spatial and temporal variability of concentration and deposition patterns, precipitation chemistry, and quality of measurements.

This paper describes analyses of daily precipitation chemistry results obtained in the Acidic Precipitation in Ontario Study (APIOS) (*3*). Although some of the results reported here are not derived through new data analysis approaches, they are about topics that are not yet conclusive. The analysis of the Ontario data was carried out to add to current knowledge so that more difinitive conclusions may be drawn. It is not our intention to give an in-depth discussion on each topic but rather deliberately to attempt to cover as many topics as possible with a large data base. The objectives of the analysis are as follows:

(1) to assess the monthly variations of precipitation chemistry